

**WHAT IS CLAIMED IS:**

1. A method of depositing a film of a metal chalcogenide, comprising the steps of:

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contacting an isolated hydrazinium-based precursor of a metal chalcogenide and a solvent having therein a solubilizing additive to form a solution of a complex thereof;

applying said solution of said complex onto a substrate to produce a coating of said solution on said substrate;

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removing said solvent from said coating to produce a film of said complex on said substrate; and thereafter

annealing said film of said complex to produce a metal chalcogenide film on said substrate.

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2. The method of claim 1, wherein said solvent is selected from the group consisting of: water, lower alcohol, ether, esters, alkylene glycol of 2-6 carbon atoms, dialkylene glycol of 4-6 carbon atoms, trialkylene glycol of 6 carbon atoms, glyme, diglyme, triglyme, propylene glycol monoacetate, DMSO, DMF, DMA, HMPA and a mixture thereof.

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3. The method of claim 2, wherein said solubilizing additive is selected from the group consisting of: an aliphatic amine of 1-10 carbon atoms, aromatic amine of 4-10 carbon atoms, aminoalcohol of 2-6 carbon atoms and a mixture thereof.

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4. The method of claim 2, wherein said solubilizing additive is selected from the group consisting of: n-propylamine, iso-propylamine, n-butylamine, sec-butylamine, iso-butylamine, pentylamine, n-hexylamine, cyclohexylamine, phenethylamine, pyridine, aniline, aminotoluene,

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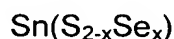


8. The method of claim 5, wherein said metal chalcogenide is represented by the formula  $M_2X_3$  wherein M is a metal selected from the group consisting of: Sb, Bi, Ga, In and a combination thereof; and wherein X is a chalcogen selected from the group consisting of: S, Se, Te and a combination thereof.

9. The method of claim 5, wherein said metal chalcogenide is represented by the formula  $M_2X$  wherein M is Tl; and wherein X is a chalcogen selected from the group consisting of: S, Se, Te and a combination thereof.

10. The method of claim 5, wherein said metal is selected from the group consisting of: Sn and Sb; and wherein said chalcogen is selected from the group consisting of: S and Se.

11. The method of claim 10, wherein said chalcogenide is represented by the formula:



wherein x is from 0 to 2.

12. The method of claim 5, wherein each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of: hydrogen, aryl, methyl and ethyl.

13. The method of claim 5, wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are hydrogen.

14. The method of claim 5, wherein said metal chalcogenide film is in the form of a thin film.

15. The method of claim 5, wherein said metal chalcogenide film comprises a polycrystalline metal chalcogenide or single crystals of said metal chalcogenide.

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16. The method of claim 15, wherein said polycrystalline metal chalcogenide has a grain size equal to or greater than the dimensions between contacts in a semiconductor device.

10 17. The method of claim 5, wherein said annealing step is carried out at a temperature and for a length of time sufficient to produce said metal chalcogenide film.

15 18. The method of claim 1, wherein said substrate is selected from the group consisting of:

Kapton, polycarbonate, silicon, amorphous hydrogenated silicon, silicon carbide (SiC), silicon dioxide (SiO<sub>2</sub>), quartz, sapphire, glass, metal, diamond-like carbon, hydrogenated diamond-like carbon, gallium nitride, gallium arsenide, germanium, silicon-germanium, indium tin oxide, boron carbide, boron nitride, silicon nitride (Si<sub>3</sub>N<sub>4</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), cerium(IV) oxide (CeO<sub>2</sub>), tin oxide (SnO<sub>2</sub>), zinc titanate (ZnTiO<sub>2</sub>), a plastic material and a combination thereof.

25 19. A film prepared by the method of claim 5.

20. The method of claim 1, wherein said hydrazinium-based precursor of said metal chalcogenide is prepared by a process comprising the steps of:

contacting: at least one metal chalcogenide and a salt of an amine compound with H<sub>2</sub>S, H<sub>2</sub>Se or H<sub>2</sub>Te, wherein said amine compound is represented by the formula:



wherein each of R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> is independently selected from the group consisting of: hydrogen, aryl, methyl, ethyl and a linear, branched or cyclic alkyl of 3-6 carbon atoms, to produce an ammonium-based precursor of  
10 said metal chalcogenide;

contacting said ammonium-based precursor of said metal chalcogenide, a hydrazine compound represented by the formula:



wherein each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is independently selected from the group consisting of: hydrogen, aryl, methyl, ethyl and a linear, branched or cyclic alkyl of 3-6 carbon atoms, and optionally, an elemental chalcogen selected from the group consisting of: S, Se, Te and a combination  
20 thereof; to produce a solution of a hydrazinium-based precursor of said metal chalcogenide in said hydrazine compound; and  
isolating hydrazinium-based precursor of said metal chalcogenide as a substantially pure product.

25 21. The method of claim 20, wherein said metal chalcogenide comprises a metal selected from the group consisting of: Ge, Sn, Pb, Sb, Bi, Ga, In, Tl and a combination thereof and a chalcogen selected from the group consisting of: S, Se, Te and a combination thereof.

22. The method of claim 20, wherein each of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  is independently selected from the group consisting of: hydrogen, aryl, methyl and ethyl.

5            23. The method of claim 20, wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  are hydrogens.

24. The method of claim 20, wherein said metal chalcogenide film is in the form of a thin film.

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25. The method of claim 20, wherein said metal chalcogenide film comprises a polycrystalline metal chalcogenide or single crystals of said metal chalcogenide.

15            26. The method of claim 25, wherein said polycrystalline metal chalcogenide has a grain size equal to or greater than the dimensions between contacts in a semiconductor device.

20            27. The method of claim 20, wherein said annealing step is carried out at a temperature and for a length of time sufficient to produce said metal chalcogenide film.

28. The method of claim 20, wherein said substrate is selected from the group consisting of:

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Kapton, polycarbonate, silicon, amorphous hydrogenated silicon, silicon carbide (SiC), silicon dioxide (SiO<sub>2</sub>), quartz, sapphire, glass, metal, diamond-like carbon, hydrogenated diamond-like carbon, gallium nitride, gallium arsenide, germanium, silicon-germanium, indium tin oxide, boron carbide, boron nitride, silicon nitride (Si<sub>3</sub>N<sub>4</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), cerium(IV)

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oxide ( $\text{CeO}_2$ ), tin oxide ( $\text{SnO}_2$ ), zinc titanate ( $\text{ZnTiO}_2$ ), a plastic material and a combination thereof.

29. A film prepared by the method of claim 20.

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30. A method of forming a field-effect transistor of the type having a source region and a drain region, a channel layer extending between the source region and the drain region, the channel layer including a semiconducting material, a gate region disposed in spaced adjacency to the channel layer, an electrically insulating layer between the gate region and the source region, drain region and channel layer, comprising:

preparing a channel layer comprising a film of a metal chalcogenide semiconducting material by a method comprising the steps of: contacting an isolated hydrazinium-based precursor of a metal chalcogenide and a solvent having therein a solubilizing additive to form a solution of a complex thereof; applying said solution of said complex onto a substrate to produce a coating of said solution on said substrate; removing said solvent from said coating to produce a film of said complex on said substrate; and thereafter annealing said film of said complex to produce a metal chalcogenide film on said substrate.

31. The method of claim 30, wherein said source region, channel layer and drain region are disposed upon a surface of a substrate, said electrically insulating layer is disposed over said channel layer and extending from said source region to said drain region, and said gate region is disposed over said electrically insulating layer.

32. The method of claim 30, wherein said gate region is disposed as a gate layer upon a surface of a substrate, said electrically insulating layer is disposed upon said gate layer, and said source region,

channel layer, and drain region are disposed upon said electrically insulating layer.

5           33.    The method of claim 30, wherein said metal chalcogenide film is in the form of a thin film having a thickness of from about 5 Å to about 2,000 Å.

10           34.    The method of claim 30, wherein said metal chalcogenide film comprises a polycrystalline metal chalcogenide or single crystals of said metal chalcogenide.

15           35.    The method of claim 34, wherein said metal chalcogenide film is polycrystalline with a grain size equal to or greater than the dimensions between contacts in a semiconductor device.

20           36.    The method of claim 30, wherein said metal chalcogenide comprises a metal selected from the group consisting of: Ge, Sn, Pb, Sb, Bi, Ga, In, Tl and a combination thereof and a chalcogen selected from the group consisting of: S, Se, Te and a combination thereof.

25           37.    The method of claim 30, wherein said annealing step is carried out at a temperature and for a length of time sufficient to produce said metal chalcogenide film.

30           38.    The method of claim 37, wherein said temperature is from about 25 °C to about 500 °C.

            39.    The method of claim 38, wherein said temperature is from about 250 °C to about 350 °C.

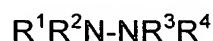


40. The method of claim 30, wherein said substrate is selected from the group consisting of:

Kapton, polycarbonate, silicon, amorphous hydrogenated silicon,  
5 silicon carbide (SiC), silicon dioxide (SiO<sub>2</sub>), quartz, sapphire, glass, metal,  
diamond-like carbon, hydrogenated diamond-like carbon, gallium nitride,  
gallium arsenide, germanium, silicon-germanium, indium tin oxide, boron  
carbide, boron nitride, silicon nitride (Si<sub>3</sub>N<sub>4</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), cerium(IV)  
oxide (CeO<sub>2</sub>), tin oxide (SnO<sub>2</sub>), zinc titanate (ZnTiO<sub>2</sub>), a plastic material  
10 and a combination thereof.

41. A field-effect transistor prepared by the method of claim 30.

42. A process for preparing an isolated hydrazinium-based  
15 precursor of a metal chalcogenide comprising the steps of:  
contacting: at least one metal chalcogenide, a hydrazine compound  
represented by the formula:



20 wherein each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is independently selected from the  
group consisting of: hydrogen, aryl, methyl, ethyl and a linear, branched or  
cyclic alkyl of 3-6 carbon atoms, and optionally an elemental chalcogen  
selected from the group consisting of: S, Se, Te and a combination  
25 thereof, to produce a solution of a hydrazinium-based precursor of said  
metal chalcogenide in said hydrazine compound; and  
isolating the hydrazinium-based precursor of said metal  
chalcogenide as a substantially pure product.

30 43. A hydrazinium metal chalcogenide prepared by the process  
of claim 42.

44. A process for preparing an isolated hydrazinium-based precursor of a metal chalcogenide comprising the steps of:

contacting: at least one metal chalcogenide and a salt of an amine compound with H<sub>2</sub>S, H<sub>2</sub>Se or H<sub>2</sub>Te, wherein said amine compound is represented by the formula:



wherein each of R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> is independently selected from the group consisting of: hydrogen, aryl, methyl, ethyl and a linear, branched or cyclic alkyl of 3-6 carbon atoms, to produce an ammonium-based precursor of said metal chalcogenide;

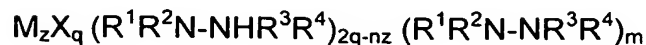
contacting said ammonium-based precursor of said metal chalcogenide, a hydrazine compound represented by the formula:



wherein each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is independently selected from the group consisting of: hydrogen, aryl, methyl, ethyl and a linear, branched or cyclic alkyl of 3-6 carbon atoms, and optionally, an elemental chalcogen selected from the group consisting of: S, Se, Te and a combination thereof; to produce a solution of a hydrazinium-based precursor of said metal chalcogenide in said hydrazine compound; and isolating hydrazinium-based precursor of said metal chalcogenide as a substantially pure product.

45. A hydrazinium metal chalcogenide prepared by the process of claim 44.

46. A hydrazinium metal chalcogenide represented by the formula:



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wherein:

M is a main-group metal having a valence n, wherein n is an integer from 1 to 6;

X is a chalcogen;

10 z is an integer from 1 to 10;

q is an integer from 1 to 30;

m is from 1 to 30.5; and

each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of: hydrogen, aryl, methyl, ethyl and a linear, branched or cyclic alkyl of 3-6 carbon atoms.

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47. The hydrazinium metal chalcogenide of claim 46, wherein said metal is selected from the group consisting of: Ge, Sn, Pb, Sb, Bi, Ga, In and Tl.

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48. The hydrazinium metal chalcogenide of claim 46, wherein said chalcogen is selected from the group consisting of: S, Se and Te.

49. A film prepared by the method of claim 1.

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